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Notes:

1. Untranslatable words are replaced with asterisks (***).
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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]A biodegradable polyester resin composition comprising:

alpha- and/or beta-hydroxycarboxylic acid unit -- more than 50 mol % -- biodegradable-polyester-resin 100 mass part to contain.

(Meta) 0.01 to acrylic ester compound 20 mass part.

[Claim 2](Meta) The biodegradable polyester resin composition according to claim 1, wherein an acrylic ester compound is a compound which has two or more acrylic (meta) groups in intramolecular, or has one or more an acrylic (meta) group, one or more glycidyl groups, or vinyl groups.

[Claim 3]The biodegradable polyester resin composition according to claim 1 or 2, wherein alpha- and/or beta-hydroxycarboxylic acid units are D-lactic acid, L-lactic acid, or these mixtures.

[Claim 4]In a time-elongational viscosity curve obtained by elongational viscosity measurement at a temperature higher 10 ** than a melting point of a biodegradable polyester resin composition, [a ratio (a_2/a_1 , strain-hardening coefficient) of the inclination a_1 to a linear zone of the extension first stage until a folding point appears, and the inclination a_2 of the extension second half after a folding point] The biodegradable polyester resin composition according to any one of claims 1 to 3, wherein strain-hardening nature which is 1.05 or more and less than 50 is revealed.

[Claim 5]The biodegradable polyester resin composition according to any one of claims 1 to 4, wherein a crystallization rate index of a biodegradable polyester resin composition is below 50 (minute).

[Claim 6]A manufacturing method of the biodegradable polyester resin composition according to any one of claims 1 to 5 carrying out melt kneading of biodegradable polyester resin, an

acrylic ester compound (meta), and the peroxide.

[Claim 7]A manufacturing method of the biodegradable polyester resin composition according to claim 6 pouring in a solution or dispersion liquid of an acrylic ester compound (meta) during melt kneading, and carrying out melt kneading of biodegradable polyester resin and the peroxide.

[Claim 8]A manufacturing method of the biodegradable polyester resin composition according to claim 6 pouring in a solution or dispersion liquid of an acrylic ester compound (meta) and peroxide during melt kneading, and carrying out melt kneading of the biodegradable polyester resin.

[Claim 9]Biodegradable resin foam produced by carrying out foaming of the biodegradable polyester resin composition according to any one of claims 1 to 5.

[Claim 10]A biodegradable resin molded body produced by carrying out injection molding of the biodegradable polyester resin composition according to any one of claims 1 to 5.

[Claim 11]A biodegradable resin molded body produced by carrying out extrusion of the biodegradable polyester resin composition according to any one of claims 1 to 5.

[Claim 12]A biodegradable resin molded body produced by carrying out blow molding of the biodegradable polyester resin composition according to any one of claims 1 to 5.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention consists of biodegradable polyester resin and an acrylic ester compound (meta), It excels in mechanical strength and a heat-resisting property, and is related with the biodegradable polyester resin composition which has rheology characteristics advantageous to shaping of the foam which does not have a problem in operability, an extrusion molding body, an injection-molding object, a blow molding object, etc., its manufacturing method and the foam obtained from it, an extrusion molding body, an injection-molding object, and a blow molding object.

[0002]

[Description of the Prior Art]While a melting point has the feature which is highly excellent in a heat-resisting property as compared with other biodegradable resin, [polylactic acid] Since there is a problem of causing foam breaking, sufficient expansion ratio not being obtained, or a bubble not being stabilized when carrying out blow molding, inflation molding or, but being easy to produce thickness deviation in a Plastic solid when melt viscosity is low, for example, carries out extrusion-foaming shaping, Severe restrictions were received in the process condition, and since the crystallization rate was slow, the manufacturing efficiency in injection molding etc. had various faults, like it is bad. Therefore, in order to present practical use, the

improvement in melt tension, and revelation of the strain-hardening nature at the time of elongational viscosity measurement and improvement in a crystallization rate were required. [0003]It is thought that the method of using the polymer which has the method of adding high-polymer polymer to make strain-hardening nature reveal generally and long-chain branching is effective. In manufacture of high-polymer polymer, since a polymerization takes a long time and productivity efficiency not only worsening but prolonged coloring, decomposition, etc. by a heat history are obtained, as for 500,000 or more biodegradable polyester, the weight average molecular weight (Mw) is not put in practical use, for example. [one side] [as a method of manufacturing branching polylactic acid] Although the method of adding a polyfunctional initiator at the time of a polymerization was known (JP,H10-7778,A, JP,2000-136256,A), after introducing branched chain at the time of a polymerization, there was a problem in respect of the ability for trouble not to occur in expenditure of resin, etc. or not change the degree of branching freely. Although the method of carrying out melt kneading of the stratified silicate is examined, there is a problem in the dispersibility of stratified silicate and it has not been put in practical use yet in biodegradable resin.

[0004]On the other hand, the method of producing bridge formation by melt kneading with peroxide, a reactive compound, etc. is [after producing biodegradable resin] simple, and many researches are done from the point that a branching degree can be changed freely. However, as for neither the acid anhydride used for JP,H11-60928,A, nor polyvalent carboxylic acid, it is practical that it is easy to produce nonuniformity in reactivity, or there is the necessity of using a reduced pressure etc. The art which reached the utilization level -- as for polyvalent isocyanate currently used for the patent No. 2571329 gazette, JP,2000-17037,A, etc. molecular weight falls easily at the time of remelting, or there is a problem in the safety at the time of operation -- is not established.

[0005]JP,H10-324766,A has disclosed if a bridge is constructed combining organic peroxide and the compound which has an unsaturated bond, it can foam to the biodegradable polyester resin compounded from the dibasic acid and the glycol effectively. This method is an example of the method of impregnating a resin particulate with these cross linking agents at a temperature lower than the melting point of resin, when divinylbenzene is used as a bridge formation assistant, are described in detail, but. (Meta) Only application to the heat-resistant low biodegradable polyester resin which is not examined about use of an acrylic ester compound, and is compounded from a dibasic acid and a glycol was considered. The method of operating stably over a long period of time was not proposed in addition of these cross linking agents or bridge formation assistants.

[0006]On the other hand, alpha- and/or beta-hydroxycarboxylic acid unit is made into a subject, and since biodegradable polyester with a high heat-resisting property has the slow crystallization rate, in various shaping processings of injection molding etc., it has the fault that

operability is bad. However, as a method of raising a crystallization rate, only the method of adding non-subtlety fine particles is examined, and radical solution is not made.

[0007]

[Problem to be solved by the invention]This invention tends to solve the above-mentioned problem and Mechanical strength, It excels in a heat-resisting property and is in providing the biodegradable polyester resin composition which has rheology characteristics advantageous to shaping of the foam which does not have a problem in operability, an extrusion molding body, an injection-molding object, a blow molding object, etc., its manufacturing method and its foam, an extrusion molding body, an injection-molding object, and a blow molding object.

[0008]

[Means for solving problem]The result of having repeated research wholeheartedly in order that this invention persons might solve such SUBJECT, With the improvement in melt viscosity, and revelation of the strain-hardening nature in elongational viscosity measurement, [the specific constituent which consists of biodegradable polyester resin and an acrylic ester compound (meta)] the obtained shaping processed goods were excellent also in a heat-resisting property or mechanical strength, found out that a crystallization rate could also solve an operable problem by it being markedly alike and improving, and it not only has rheology characteristics excellent in foaming nature, but they reached this invention.

[0009]That is, the gist of this invention is as follows.

(1) alpha- and/or beta-hydroxycarboxylic acid unit -- more than 50 mol % -- the biodegradable polyester resin composition for foaming which consists of biodegradable-polyester-resin 100 mass part to contain and 0.01 to acrylic ester compound (meta-) 20 mass part.

(2) alpha- and/or beta **HIDOROKISHI carboxylic acid units -- more than 50 mol % -- the manufacturing method of the biodegradable polyester resin composition carrying out melt kneading of biodegradable polyester resin, the acrylic ester compound (meta-), and organic peroxide to contain.

(3) alpha- and/or beta **HIDOROKISHI carboxylic acid units -- more than 50 mol % -- the biodegradable resin foam produced by fabricating the biodegradable polyester resin composition which consists of biodegradable polyester resin to contain and an acrylic ester compound (meta-), an extrusion molding body, an injection-molding object, and a blow molding object.

[0010]

[Mode for carrying out the invention]in this invention -- biodegradable polyester resin -- alpha- and/or beta-hydroxycarboxylic acid unit -- more than 50 mol % -- to contain is required. As an alpha- and/or beta-hydroxycarboxylic acid unit, D-lactic acid, L-lactic acid or these mixtures, glycolic acid, 3-hydroxybutyric acid, 3-HIRODOKISHI valeric acid, 3-hydroxy caproic acid, etc. are mentioned. Since biodegradable polyester resin containing D-lactic acid, L-lactic acid, or

these mixtures is excellent in mechanical strength and a heat-resisting property, it is preferred. The content of these alpha- and/or beta-hydroxycarboxylic acid unit needs to be more than 50 mol %. There is a problem that a biodegradable heat-resisting property falls that content is less than [50 mol %]. therefore, biodegradable polyester resin of this invention -- polylactic acid, polyglycolic acid, poly (3-hydroxybutyric acid), poly (3-HIRODOKISHI valeric acid), poly (3-hydroxy caproic acid), these copolymers, these mixtures, etc. -- more than 50 mol % -- it contains.

[0011]The biodegradable polyester resin used here uses a solid-state-polymerization method together to a publicly known melt polymerization method or a pan, and is usually manufactured. About poly (3-hydroxybutyric acid) and poly (3-HIRODOKISHI valeric acid), production by a microorganism is also possible.

[0012]alpha- used for this invention, and/or beta-hydroxycarboxylic acid unit -- more than 50 mol %, [the biodegradable polyester resin to contain] In the range which does not spoil sharply a poly (alpha- and/or beta-hydroxycarboxylic acid) heat-resisting property, necessity can be accepted, and other biodegradable resinous principles can also be copolymerized or mixed. The aliphatic polyester which consists of diol represented by poly (ethylene succinate), poly (butylene succinate), etc. and dicarboxylic acid as other biodegradable resin, The poly represented by poly (epsilon-caprolactone) (omega-hydroxy alkanoate), Polysaccharide, such as polyester amide, polyester carbonate, a starch, etc. besides the poly (butylene succinate co-butylene terephthalate) which shows biodegradation even if the aromatic component is furthermore included, etc. are mentioned (butylene horse mackerel *****- co-butylene terephthalate).

[0013]Although there is no restriction in particular as molecular weight of the biodegradable polyester resin used by this invention, it is preferred that a weight average molecular weight is less than [50,000 or more] 1 million, and it is preferred that it is [or more further 100,000] less than 1 million. Since the melt viscosity of a resin composition is too low when a weight average molecular weight is less than 50,000, it is not desirable. On the contrary, since the moldability of a resin composition falls quickly when this exceeds 1 million, it is not desirable.

[0014][as an acrylic ester compound used by this invention (meta)] The compound which reactivity with biodegradable resin is high and a monomer cannot remain easily, has two or more acrylic (meta) groups in intramolecular since there is comparatively little toxicity and coloring of resin also has it, or has one or more an acrylic (meta) group, one or more glycidyl groups, or vinyl groups is preferred. [little] As a concrete compound, glycidyl methacrylate, glycidyl acrylate, Glycerol dimethacrylate, trimethylolpropanetrimethacrylate, Trimethylolpropane triacrylate, allyloxy polyethylene glycol monoacrylate, Allyloxy polyethylene glycol monomethacrylate, polyethylene glycol dimethacrylate, Polyethylene glycol diacrylate, polypropylene glycol dimethacrylate, The copolymer of the alkylene of various length may be

sufficient as polypropylene glycol diacrylate, polytetramethylene glycol dimethacrylate, and these alkylene glycol parts, and butanediol methacrylate, butanediol acrylate, etc. are mentioned further.

[0015](Meta) The loadings of an acrylic ester compound are 0.05 to 10 mass part preferably 0.01 to 20 mass part to biodegradable-polyester-resin 100 mass part. In less than 0.01 mass parts, when the improvement effect of mechanical strength, a heat-resisting property, and dimensional stability made into the purpose of this invention is not acquired but it exceeds 20 mass parts, the degree of bridge formation is too strong, and in order that trouble may occur in operability, it is not desirable.

[0016][the biodegradable polyester resin composition in this invention] In the logarithm plot (refer to drawing 1) of the time-extension viscosity obtained by extension viscosity measurement at a temperature higher 10 ** than the melting point, It is preferred that strain-hardening [of as / whose strain-hardening coefficients denoted by the ratio (a_2/a_1) of the inclination a_1 to the linear zone of the extension first stage until a folding point appears, and the inclination a_2 of the extension second half after a folding point are 1.05 or more and less than 50] nature is revealed. More desirable strain-hardening coefficients are 1.5-30. Foam breaking is caused at the time of extrusion-foaming shaping as a strain-hardening coefficient is less than 1.05, or it is easy to produce thickness deviation in a Plastic solid. Flowability also falls greatly and is not [that it is it easy to generate a gel that a strain-hardening coefficient is 50 or more at the time of shaping] preferred.

[0017]In a DSC device, once carrying out melting of the biodegradable polyester resin composition of this invention at 200 **, it is preferred that a crystallization rate index when carrying out isothermal crystallization at 130 ** is below 50 (minute). A crystallization rate index is shown in time (minute) (refer to drawing 2) until it reaches 1/2 of the crystallinity which finally reaches, when crystallizing resin at 130 ** from a 200 ** molten state, and it means that a crystallization rate is so quick that an index is small. If a crystallization rate index is higher than 50 (minute), the shape of the Plastic solid which crystallizing takes time too much and is wished to have will not be acquired, or the cycle time in injection molding etc. will become long, and productivity will worsen. As for the minimum of a crystallization rate index, since moldability will worsen if a crystallization rate is too quick, it is preferred that it is 0.1 (minute) grade. A crystallization rate index becomes so small that the amount of cross linking agents and/or the amount of peroxide increase, and can make a crystallization rate quick. If 0.1-5 mass % addition of non-subtlety powder, such as a talc and calcium carbonate, is done, it can be made quicker by a synergistic effect. It can be made so quick that the functional group number of a cross linking agent is furthermore increased.

[0018]By using as a raw material biodegradable polyester resin, an acrylic ester compound (meta), and the peroxide mentioned later, using a common extruder, melt kneading of the

biodegradable polyester resin composition of this invention can be carried out, and it can be manufactured. It is preferred to use the extruder of two axes in the meaning which improves a kneading state. kneading temperature -- the range of - (+5 ** of melting points of resin) (+100 ** of melting points of resin) -- as for kneading time, 20 seconds - 30 minutes are preferred. Kneading and reacting become insufficient in case of low temperature or a short time from this range, and decomposition and coloring of resin may break out in case of high temperature or a long time. In this case, if they are a solid state, their method of supplying using a dry blend or a fine-particles feeder is desirable, and when it is a liquid state, the method of pouring in from the middle of an extruder using a pressurization pump is desirable [the acrylic ester compound and peroxide which are used by this invention (meta)]. when it dissolves or distributes through an acrylic ester compound (meta-) and/or peroxide and pours into a kneading machine especially, operability is markedly easy coming to be alike, and desirable. Namely, biodegradable polyester resin and peroxide, [during melt kneading] (Meta) It is preferred to pour in the solution or dispersion liquid of an acrylic ester compound, or to pour in the solution or dispersion liquid of an acrylic ester compound (meta) and peroxide during melt kneading, and to carry out melt kneading of the biodegradable polyester resin.

[0019](Meta) Although what that dissolves or distributes an acrylic ester compound and/or peroxide is common as a medium is used and it is not limited in particular, the plasticizer excellent in compatibility with aliphatic polyester of this invention is preferred, and a biodegradable thing is preferred. For example, one or more sorts of plasticizers etc. which were chosen from an aliphatic-polycarboxylic-acid ester derivative, an aliphatic-polyhydric-alcohol ester derivative, an aliphatic series oxy ester derivative, an aliphatic polyether derivative, an aliphatic polyether polyvalent-carboxylic-acid ester derivative, etc. are mentioned. As a concrete compound, dimethyl horse mackerel PETO, dibutyl horse mackerel PETO, triethylene glycol diacetate, methyl acetyl ricinolate, acetyl tributyl citric acid, polyethylene glycol, dibutyl diethylene glycol succinate, etc. are mentioned. As amount of the plasticizer used, 30 or less mass parts are preferred to resin amount 100 mass part, and 0.1 to 20 mass part is still more preferred. When the reactivity of a cross linking agent is low, it is not necessary to carry out the amount used of the plasticizer but, and when reactivity is high, it is preferred to use 0.1 or more mass parts. An acrylic ester compound (meta) and peroxide may be poured in separately.

[0020]As an example of the peroxide used by this invention, organic peroxide with good dispersibility has it, and specifically, [preferred] Benzoyl peroxide, bis(butylperoxy) trimethylcyclohexane, Bis(butylperoxy)cyclo dodecane, butyl bis(butylperoxy)valerate, Dicumyl peroxide, butylperoxy benzoate, dibutyl peroxide, bis(butylperoxy)diisopropylbenzene, dimethyldi (butylperoxy) hexane, dimethyldi (butylperoxy) hexyne, butylperoxy cumene, etc. are mentioned.

[0021]The loadings of peroxide are 0.1 to 10 mass part preferably 0.1 to 20 mass part to biodegradable-polyester-resin 100 mass part. The improvement effect of mechanical strength, a heat-resisting property, and dimensional stability made into the purpose of this invention in less than 0.1 mass parts is not acquired, but in exceeding 20 mass parts, it becomes unused, and it is not desirable at a cost aspect.

[0022]Although the biodegradable polyester resin composition of this invention can carry out melt kneading of these and can manufacture them as mentioned above by using biodegradable polyester resin, an acrylic ester compound (meta), and peroxide as a raw material, [the biodegradable polyester resin composition] Generally, in order to decompose during melt kneading, peroxide does not always necessarily contain peroxide in the obtained resin composition. Although it is preferred to use media, such as a plasticizer, when adding an acrylic ester compound (meta) and/or peroxide, since this medium may also volatilize at the time of melt kneading, the medium does not always necessarily contain in the obtained resin composition.

[0023]Unless the characteristics are greatly spoiled to the biodegradable polyester resin composition of this invention, it is also possible to add a pigment, a thermostabilizer, an antioxidant, a weathering agent, a flame retarder, a plasticizer, lubricant, a release agent, an antistatic agent, a filler, etc. further. As a thermostabilizer or an antioxidant, hindered phenols, phosphorus compounds, hindered amine, sulfur compounds, a copper compound, halide of an alkali metal, or these mixtures can be used, for example. As an inorganic filler, a talc, calcium carbonate, zinc carbonate, wollastonite, Silica, alumina, magnesium oxide, a calcium silicate, sodium aluminate, Calcium aluminate, sodium aluminosilicate, a magnesium silicate, A glass balloon, carbon black, zinc oxide, antimony trioxide, zeolite, a hydrotalcite, a metal fiber, a metal whisker, a ceramic whisker, potassium titanate, boron nitride, graphite, glass fiber, carbon fiber, etc. are mentioned. as an organic filler -- starch, a cellulose particulate, wood flour, tofu lees, and unhulled rice -- the polymer which exists in nature, such as husks and wheat bran, and such denaturation articles are mentioned.

[0024]The method in particular of mixing the above-mentioned additive and other thermoplastics to the biodegradable polyester resin composition of this invention is not what is limited, It is good to knead by the kneading method using a 1 axis extruder, a twin screw extruder, a roll kneading machine, Brabender, etc. which are known from before after the usual heat melting. It is also effective to use a static mixer and a dynamic mixer together. It may add at the time of the polymerization of biodegradable resin.

[0025]All general methods are applicable to the foaming method at the time of manufacturing foam from the biodegradable polyester resin composition of this invention. For example, it extrudes from a slit shaped nozzle, and the decomposable blowing agent beforehand disassembled into resin with the melting temperature of resin is blended using the extruder,

and it can be made [it can be made a sheet shaped, or can extrude from a round shape nozzle, and] strand shape. The azo compound represented by an azodicarbonamide and barium azo dicarboxylate as an example of decomposed type foam, The nitroso compound represented by N,N'-dinitrosopentamethylenetetramine, The foaming agent etc. of inorganic systems, such as a hydrazine compound represented by a 4,4'-oxyscrew (benzenesulphonyl hydrazide) and HIDORAJI carvoneamide or sodium hydrogencarbonate, can be mentioned. It is also possible to pour in a volatilized type foaming agent and to foam to it from the extruder middle. As a foaming agent in this case, the organic solvent etc. which are represented by various alcohols, such as various hydrocarbons, such as inorganic compounds, such as nitrogen, carbon dioxide, and water, methane, ethane, butane, a chlorofluorocarbon compound, ethanol, and methanol, can be mentioned. After impregnating with the foaming agent which produced the particles of the resin composition beforehand and was shown in the above, such as an organic solvent and water, the method of making it foam by change of temperature or a pressure, and producing foaming particles is also applicable.

[0026]Next, the extrusion method at the time of manufacturing an extrusion molding body from the biodegradable polyester resin composition of this invention is described. As an extrusion method, a T die method and the circle Di method are applicable. Extrusion temperature needs to be more than the melting point (T_m) of a biodegradable polyester resin composition, or flow beginning temperature, and the range of it is 190-220 °C still more preferably 180-230 °C preferably. Since the problem of shaping becoming unstable if a molding temperature is too low, or biodegradable polyester resin decomposing and the hardness of the extrusion molding body obtained falling, if it is easy to fall into an overload and a molding temperature is too high conversely, or coloring occurs, it is not desirable. By extrusion, although a biodegradable sheet, a pipe, etc. are producible, more than the glass transition temperature (T_g) of a biodegradable polyester resin composition can also heat-treat below (T_m-20 °C) in order to improve these heat-resisting properties.

[0027]As a concrete use of the biodegradable sheet or pipe manufactured by an extrusion method, curd, such as an original fabric sheet for deep-drawing shaping, an original fabric sheet for batch type foaming, and a credit card, an underlay, a clear file, a straw, hard agriculture, the pipe for horticulture, etc. are mentioned. The biodegradable sheet can manufacture the container for foodstuffs, agriculture and the container for horticulture, a blister pack container, a press through pack container, etc. by performing deep-drawing shaping of vacuum forming, pressure forming, vacuum pressure sky shaping, etc. As for a deep-drawing molding temperature and heat treatment temperature, it is preferred that it is - (T_g+20 °C) (T_m-20 °C). If deep drawing may become difficult in the following (T_g+20 °C), or deep-drawing temperature may become insufficient [the heat-resisting property of the container obtained] and deep-drawing temperature exceeds (T_m-20 °C) conversely, thickness deviation may arise,

or an orientation may collapse and shock resistance may fall.

[0028]Although the form in particular of the container for foodstuffs, agriculture and the container for horticulture, a blister pack container, and a press through pack container is not limited, in order to accommodate foodstuffs, an article, medicine, etc., it is preferred that deep drawing is carried out to a depth of not less than 2 mm. Although the thickness in particular of a container is not limited, it is preferred from a powerful point that it is not less than 50 micrometers, and it is more preferred that it is 150-500 micrometers. As a concrete example of the container for foodstuffs, the tray of a perishable food, an instant food container, a fast food container, a lunch box, etc. are mentioned. A seedling raising pot etc. are mentioned as an example of agriculture and the container for horticulture. As a concrete example of a blister pack container, the container of various commodity groups, such as stationery, a toy, and a dry battery, is mentioned besides foodstuffs.

[0029]Next, the blow molding method at the time of manufacturing a blow molding object from the biodegradable polyester resin composition of this invention is described. As a blow molding method, the direct blowing method which fabricates directly from a raw material chip, the injection-blow-molding method injection molding performs blow molding first after fabricating a preforming object (closed-end parison), extension blow molding, etc. are employable. Any method of the hot parison method for performing blow molding succeeding the preforming object shaping back and the cold parison process which heats again and performs blow molding once it cools and takes out a preforming object is employable. Blow molding temperature needs to be $-(T_g+20^{\circ}\text{C})$ $(T_m-20^{\circ}\text{C})$. Since problems, such as thickness deviation arising or carrying out blowdown due to a viscosity fall, will occur if shaping may become difficult, or blow molding temperature may become insufficient [the heat-resisting property of the container obtained] in the following $(T_g+20^{\circ}\text{C})$ and blow molding temperature exceeds $(T_m-20^{\circ}\text{C})$ conversely, it is not desirable.

[0030]Next, general injection molding process can be used as injection molding process at the time of manufacturing an injection-molding object from a biodegradable polyester resin composition of this invention, and gas ejection shaping, injection press forming, etc. can be adopted further. Cylinder temperature at the time of injection molding needs to be more than T_m or flow beginning temperature, and a range of it is $190-220^{\circ}\text{C}$ still more preferably $180-230^{\circ}\text{C}$ preferably. Since short-circuit will occur if a molding temperature is too low, and a problem of shaping becoming unstable, or biodegradable polyester resin decomposing and hardness of a Plastic solid acquired falling, if it is easy to fall into an overload and a molding temperature is too high conversely, or coloring occurs, shaping is not preferred. On the other hand, it is necessary to make tool temperature into below $(T_m-20^{\circ}\text{C})$. When promoting crystallization within a metal pattern in order to improve the heat-resisting property of biodegradable polyester resin, $(T_g+20^{\circ}\text{C})$ It is preferred to cool below to T_g , after maintaining predetermined

time by - ($T_m - 20$ °C), and when back-crystallizing conversely, after cooling below to T_g directly, it is preferred to heat-treat by $T_g - (T_m - 20$ °C) again.

[0031] A form in particular of an injection-molded product manufactured by the above-mentioned injection molding process is not limited, but, [as an example] Tableware, such as a pan, a bowl, a bowl, chopsticks, a spoon, a fork, and a knife, a container for fluids, Stationery, such as cap for containers, ruler, pens-and-pencils, clear case, and CD case, Daily necessities, such as a sink-corner strainer for kitchens, a garbage can, a washbasin, a toothbrush, a comb, and a hanger, Resin part articles for cars, such as resin part articles for electric appliances, such as various toys, such as agriculture and materials for horticulture, such as a flowerpot and a seedling raising pot, and a plastic model, an air-conditioner panel, a refrigerator tray, and various cases, a bumper, an instrument panel, and a door trim, etc. are mentioned. Although a form in particular of a container for fluids is not limited, in order to accommodate a fluid, it is preferred to be fabricated by depth of not less than 20 mm. Although thickness in particular of a container is not limited, it is preferred from a powerful point that it is 0.1 mm or more, and it is more preferred that it is 0.1-5 mm. As an example of a container for fluids, containers, such as a momentary preservation container of seasonings, such as cap for drinks, such as dairy products, soft drinks, liquor, and a bottle for drinks, soy sauce, a source, mayonnaise, catsup, and an edible oil, and shampoo rinse, a container for cosmetics, a container for agricultural chemicals, etc. are mentioned.

[0032]

[Working example] Although an embodiment explains this invention still more concretely below, this invention is not limited only to an embodiment.

[0033] The measuring method used for evaluation of an embodiment and a comparative example is as follows.

- (1) Molecular weight : it asked by standard polystyrene conversion at 40 °C by making tetrahydrofuran into an eluate using the gel permeation chromatography (GPC) device (made by Shimadzu) provided with the differential refractive index detector.
- (2) The rate of bending flexibility : the 150mmx10mmx6mm specimen was produced according to ASTM-790, load was applied by a part for 1 mm of deformation velocity/, and the rate of bending flexibility was measured.
- (3) Melting point : it measured on condition of for heating-rate/of 10 °C using differential scanning calorimeter DSC-7 (made by PerkinElmer, Inc.).
- (4) According to MFR:JIS K7210, it measured on condition of F of the attached document A table 1.
- Elongational viscosity : (5) After producing a 60mmx7mmx1mm specimen and supporting the both ends by a metal belt clamp using the elongational viscosity measuring apparatus RME (made in Leo Mettrick), [a temperature higher 10 °C than the melting point of a resin

composition] It was made to rotate by distortion velocity [of 0.1 sec]⁻¹, extension modification was added to the measurement sample, and it asked for elongational viscosity by detecting the torque which starts during modification at a pinch roller.

(6) Strain-hardening coefficient (a_2/a_1) (refer to drawing 1) : in the log-log plot of extension time and elongational viscosity, the ratio (a_2/a_1) of the inclination a_1 to the linear zone of the extension first stage until a folding point appears, and the inclination a_2 of the extension second half after a folding point was computed.

(7) Crystallization rate index (refer to drawing 2)

It holds for 5 minutes at 200 °C after 20 °C → 200 °C (a part for +500 °C/), and it held at 130 °C and was made to crystallize after a temperature fall using a DSC device (Pyris1 DSC by PerkinElmer, Inc.) at 200 °C → 130 °C (a part for -500 °C/). When crystallinity which finally reaches was set to 1, the time when crystallinity amounted to 0.5 was found as a crystallization rate index (minute).

(8) Expansion ratio : once drying the pellet of a biodegradable polyester resin composition, use a liquefied carbon dioxide as a foaming agent, and it is a batch foaming examination (). [using a resisting pressure container] [a temperature lower 10 °C than a melting point] And it returned carbon dioxide to ordinary pressure after being impregnated by 10MPa, continuation foaming sheet production experiments (2 axis extruding press machine PCM-30 (the IKEGAI make, Di's slit 40 mm in length, and slit 1 mm in width) is used, and they are extrusion head temperature; 200 °C and Di outlet temperature; 160 °C) were conducted. It computed from the ratio of the volume which increases when the obtained foam is immersed underwater, and the mass of foam and the volume which can be found from a resin density.

(8) foam appearance: -- O: -- it becomes the shape of a uniform rod and there is no surface dry rough skin.

**: Although it becomes the shape of an uneven rod in part, there is no surface dry rough skin.

x: It becomes the shape of an uneven rod and is surface dry-rough-skin ****.

(9) Using the evaluation injection-molding device (Toshiba Machine IS-100E) of injection-molding nature, injection molding was performed to the mold release cup type (38 mm in diameter, and 300 mm in height) (the molding temperature of 200 °C, the tool temperature of 15 °C), and cycle time until it can release a cup from mold good was investigated.

(10) The evaluation blow molding device (Nissei Ey S&B, INC. make ASB-50HT) of blow molding nature is used, This was warmed in skin temperature of 80 °C with the molding temperature of 200 °C after producing yellowtail form (30 mm in diameter, 100 mm in height, and 3.5 mm in thickness), and blow molding was performed to the bottle-shaped metal pattern (90 mm in diameter, and 250 mm in height). The appearance of the Plastic solid with a thickness of 0.35 mm obtained was evaluated.

O : it is good and is as the purpose.

** : Although it has fabricated mostly as the purpose, they are those with fault in part.

x : It was not able to fabricate as the purpose.

xx : Shape was not taken at all.

[0034] The raw material used for the embodiment and the comparative example is as follows.

(1) biodegradable-polyester-resin: -- A: -- polylactic acid (the weight average molecular weight 200,000, 99% of L object, 1% of D object, the crystallization rate index 95)

B: Polylactic acid (weight average molecular weight 180,000, 90% of L object, 10% of D object, and crystallization rate index >100)

C: Polylactic acid (weight average molecular weight 180,000, 80% of L object, 20% of D object, and crystallization rate index >100)

D: Polylactic acid (weight average molecular weight 90,000, 85% of L object, 15% of D object, and crystallization rate index >100)

(2) (meta-) -- acrylic ester compound: -- PEGDM: -- polyethylene glycol dimethacrylate (made by Nippon Oil & Fats)

TMPTM: Trimethylolpropanetrimethacrylate (made by Nippon Oil & Fats)

PEGDA: Polyethylene glycol diacrylate (made by Nippon Oil & Fats)

GM: Glycidyl methacrylate (made by Nippon Oil & Fats)

(3) Peroxide : I: di-t-butyl peroxide (made by Nippon Oil & Fats)

J: 2,5-dimethyl- 2,5-bis(tert-butyl peroxide)hexyne- 3 (it dissolved and used so that it might become a solution 10% at the acetyl tributyl citric acid which is the Nippon Oil & Fats make and a plasticizer.)

K: Inactive solid dilution fine particles of the 2,5-dimethyl- 2,5-bis(tert-butyl peroxide)hexyne- 3 (the dry blend was beforehand carried out to the Nippon Oil & Fats make and biodegradable polyester resin, and it used for them.)

[0035] Polylactic acid (99% of L object, 1% of D object) (A) 100 mass part of the weight average molecular weight 200,000 was supplied using the embodiment 1 2 axis extruding press machine (IKEGAI PCM-30, dice diameter; 4-mm x 3 hole, extrusion head temperature; 200 **, Di outlet temperature; 180 **). Talc (wood formation make) 0.5 mass part was added as a foaming nucleating additive. The solution which dissolved polyethylene-glycol-dimethacrylate (made by Nippon Oil & Fats) (PEGDM) 2 mass part and di-t-butyl peroxide (made by Nippon Oil & Fats) (I) 2 mass part in plasticizer acetyl tributyl citric acid 5 mass part using the pump from the kneading machine middle is poured in and extruded, It was processed into the pellet type and the biodegradable polyester resin composition was obtained. The physical properties of the obtained constituent and the result of the foaming examination were shown in Table 1.

[0036] Except having changed Embodiments 2-12, the comparative example 1 - 7

biodegradable polyester resin, an acrylic ester compound (meta), and peroxide into a kind and quantity which are shown in Table 1, respectively, a constituent was obtained like Embodiment

1 and a foaming examination was done. The physical properties of an obtained constituent and a result of a foaming examination were shown in Table 1. [conditions indicated to the valuation method (9) and (10) using a biodegradable polyester resin composition obtained by Embodiments 4, 6, 9, and 12 and the comparative examples 1, 2, and 7] A bottle-shaped (90 mm in diameter, 250 mm in height, and 0.35 mm in thickness) blow molding object was acquired for a mold release cup type (38 mm[in diameter] x300 mm in height) injection-molding object again. An evaluation result of injection-molding nature and blow molding nature was summarized in Table 1.

[0037]When pouring comparative example 8 polyethylene glycol dimethacrylate (PEGDM) and di-t-butyl peroxide (I) into a kneading machine with a pump, carried out like Embodiment 1 except not having used plasticizer acetyl tributyl citric acid, but. It becomes impossible for piping to have got blocked and sent the liquid 10 minutes after the pump liquid-sending start, and a resin composition was not able to be obtained.

[0038]

[Table 1]

		生分解性ポリエステル樹脂組成物の原料					組成物の物性						発泡体の物性			成形体		
		生分解性ポリエステル樹脂		(メタ)アクリル酸エステル化合物		過酸化剤		樹脂分子量	曲げ弾性率	融点	MFR	歪み硬化係数	結晶化速度指数	発泡倍率		外観	射出成形サイクル(秒)	ブロー成形性
		種類	種類	質量部	種類	質量部	(Mw)*							(MPa)	(℃)			
実施例	1	A	PEGDM	2	I	2	—	4150	169	7.8	2.7	0.9	14	10	○	—	—	
	2	A	PEGDM	1	I	0.5	283200	4070	167	20.3	2.1	1.5	10	7	○	—	—	
	3	A	PEGDM	0.25	I	1	234800	3780	163	26.8	2.0	1.4	10	8	○	—	—	
	4	A	PEGDM	0.25	I	0.15	215600	3560	163	29.0	2.2	1.4	8	7	○	23	△	
	5	A	TMPTM	2	I	2	—	3980	169	8.9	3.0	1.0	16	12	○	—	—	
	6	A	PEGDA	0.25	I	1	242300	3580	168	18.9	1.9	1.2	11	9	○	22	○	
	7	A	GM	2	I	2	—	3940	169	7.5	2.8	0.9	22	16	○	—	—	
	8	A	PEGDM	1	J	0.5	290100	3770	164	18.8	2.1	1.3	13	10	○	—	—	
	9	A	PEGDM	0.25	K	1	223300	3690	163	24.5	1.8	1.2	12	8	○	19	○	
	10	B	PEGDM	1	I	0.5	192300	3250	156	30.3	2.4	1.8	18	16	○	—	—	
	11	C	PEGDM	1	I	0.5	189000	3040	示さず*	32.5	2.1	2.0	21	18	○	—	—	
	12	D	PEGDM	1	I	0.5	101100	3010	示さず*	38.7	1.7	1.1	15	12	○	17	○	
比較例	1	A	—	0	I	2	203000	3210	165	50.2	測定不可	67	1.2	1.1	× (破泡)	38	×	
	2	A	PEGDM	2	—	0	200200	3060	166	52.8	測定不可	85	1.3	1.2	× (破泡)	45	×	
	3	B	—	0	I	0.5	183200	2950	154	63.4	1.0	>100	2.5	1.8	△	—	—	
	4	C	—	0	I	0.5	182100	2780	示さず*	65.9	1.0	>100	2.4	1.5	△	—	—	
	5	D	—	0	I	0.5	90100	2830	示さず*	87.2	測定不可	>100	2.2	1.6	△	—	—	
	6	A	PEGDM	21	I	21	—	—	170	測定不可	測定不可	0.05	—	—	—	—	—	
	7	A	—	0	—	0	195000	2600	168	45.5	測定不可	110	1.2	1.1	×	76	×	

* : —は樹脂が溶媒に溶けなかったことを示す。

[0039]It turned out that it excels in the rate of bending flexibility in Embodiments 1-9 so that clearly from Table 1, and uniform foam is obtained by independent foaming. In Embodiments 10-12, it turned out that it excels in the rate of bending flexibility even if it changes biodegradable resin, and uniform foam is obtained by independent foaming. The Plastic solid with a crystallization rate quick [the resin composition of an embodiment], and blow molding either good injection molding process or method was able to be acquired. In the comparative

example 1 and the comparative examples 3-5, since the acrylic ester compound (meta) was not contained, an improvement of the mechanical strength which makes the rate of bending flexibility representation could not be aimed at, but the strain-hardening coefficient was also low. In these resin, even if it performed foaming treatment, satisfactory foam was not obtained. In the comparative example 2, since peroxide is not used as a raw material, an improvement of the mechanical strength which makes the rate of bending flexibility representation cannot be aimed at, and a modulus of strain hardening cannot be measured, either. Although it was going to obtain the foam of the resin, foam breaking was not able to be carried out and satisfactory foam was not able to be obtained. In the comparative example 6, bridge formation progressed too much, the jam occurred in the middle of the extruder, and a resin composition was not able to be obtained.

[0040]To the biodegradable resin composition obtained in embodiment 13 Embodiment 2, the dry blend was carried out and the foaming examination was done so that an azodicarbonamide system heat decomposition type blowing agent (Nagakazu formation make BINIHORUAC#3) might become 1.5 mass % as a foaming agent. That is, the film was produced using the extrusion T Di testing machine (3.5 steps of SURUZA type static mixer juxtaposition, slit length of 500 mm, slit width of 1.5 mm) of the diameter of 40 mm of one axis by a part for 3-m/in the melting temperature of 220 **, the Di outlet temperature of 160 **, 16 rpm of screw rotation speed, and taking over velocity. The foaming state at the time of film production is very uniform, the expansion ratio of the obtained foam is four, and it comprises independent type air bubbles.

[0041]The foaming examination was done like Embodiment 13 except having extruded liquefaction carbon dioxide with the high-pressure pump, and having poured it in from the extruder middle as embodiment 14 foaming agent, so that it might become 3 mass % of biodegradable resin resin. The foaming state at the time of film production is very uniform, the expansion ratio of the obtained foam is 12, and it comprises independent type air bubbles.

[0042]Freezing grinding of the biodegradable resin composition obtained in embodiment 15 Embodiment 2 was carried out, and the grain with a mean particle diameter of 1 mm was produced. Once drying this grain, the batch foaming examination (carbon dioxide is returned to ordinary pressure after being impregnated by 10MPa at a temperature lower 10 ** than a melting point using a resisting pressure container) was done using a liquefied carbon dioxide as a foaming agent. The obtained foaming grains are very uniform, the expansion ratio is 35, and it comprises independent type air bubbles.

[0043]

[Effect of the Invention]According to this invention, [the biodegradable polyester resin composition which is excellent in mechanical strength and a heat-resisting property, and has rheology characteristics advantageous to shaping of foam etc.] Simple, cost can also be

produced low and can provide the foam which was excellent in fizz using this resin, the injection-molding object excellent in moldability, a blow molding object, and an extrusion molding body.

[Translation done.]